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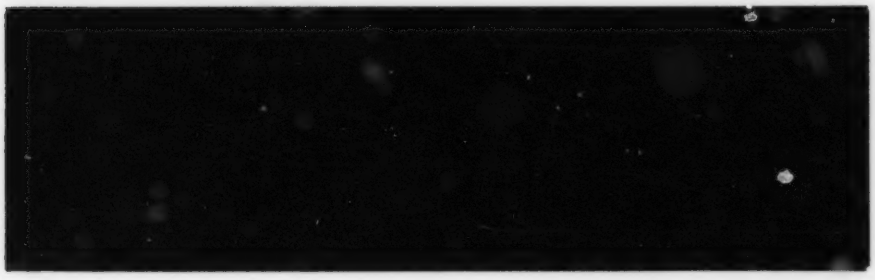

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CERCHAR Final Report

CANMET Contract No. 23440-1-9166/01-SQ

# STUDY TO EVALUATE PATENTED HYDRATION TECHNOLOGY

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MICROMEDIA

# CERCHAR Final Report

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## STUDY TO EVALUATE PATENTED HYDRATION TECHNOLOGY

### INTRODUCTION

Ash disposal and improvement of the efficiency of sulphur capture of limestone used in fluidized bed combustors (FBC) remain two major issues for this advanced combustion technology. Recently, the French organization, CERCHAR, has developed a patented technology for hydrating ashes from processes like FBC with high calcium content. This patented hydration technology permits complete hydration of the CaO component without conversion of the CaSO4 component to gypsum or the formation of ettringite.

Complete hydration of the circulating FBC ashes has hitherto proved impossible and conventional hydration techniques also cause the formation of compounds like ettringite. Incomplete hydration, the formation of aluminosilicates and compounds like ettringite are all potential causes of dimensional instability which impair the disposal characteristics of circulating FBC ashes. In addition, the possibility of utilization of ashes is reduced by the formation of ettringite. Further, the efficiency of processes designed to reuse spent sorbent are also diminished rendering them uneconomic, an effective hydration process offers the possibility of allowing reuse of spent sorbent with major savings resulting in terms of purchase and transportation of limestone and subsequent disposal costs for solid residues from the process. Another possible use of the technology is to provide ashes suitable for use with another advanced technology for producing pumpable slurries for mine backfill, known as AWDS and for which the unhydrated CFBC ashes present a considerable problem.

The degree of hydration achieved by the CERCHAR processes has been examined in a recent contract carried out for CANMET by the University of Toronto [Iribarne, 1991] and the preliminary results appear extremely promising. In order for the CERCHAR processes to be examined in further detail, it is necessary to hydrate a larger quantity of ashes (200 kg) to permit further work on these ashes. These ashes were produced in a $93k circulating FBC trial carried out on ERL-CANMET's pilot-scale CFBC combustor, which was co-funded by Environment Canada and Nova Scotia Power Corporation.

Successful demonstration of the CERCHAR processes offers the possibility of significantly improving the commercial potential of circulating FBC technology. This work may also assist Nova Scotia Power Corporation with their 165 MWe circulating FBC boiler project, which is due to be commissioned in 1993 at Point Aconi and which will cost approximately $500 million.

## CERCHAR HYDRATION TREATMENT

200 kg of CFBC ashes supplied by CANMET were treated in Feb./March 92 by the CERCHAR hydration technique (described in patent WO 91/10628 - PCT/FR91/00027) in about 3-5 kg batches, using its 20 litre capacity pilot plant.

CANMET provided CERCHAR with 3 different kinds of ashes produced from runs with Devco Prince coal and Calpo limestone on the ERL-CANMET's pilot-scale CFBC combustor :
- the first and the second ashes were from a run (labelled PC1) taking place on Dec. 6/91 between the hours of 0:00 and 12:00. The first ashes were bed ashes extracted from the bed at the end of the run. The second ashes were fly ashes captured by the baghouse filters.
- the third ashes were from a run (labelled PC3) on Jan. 30/92 between the hours 3:00 and 16:00.

At the CERCHAR laboratories, each one of the ashes was sampled after having mixed the pails containing the same quality :

bed ashes (PC1) = CERCHAR sample reference 9741
fly ashes (PC1) = CERCHAR sample reference 9744
fly ashes (PC3) = CERCHAR sample reference 9749

The hydration working conditions comprised a first stage in which the ashes, at ambient temperature, put into the pilot plant were wetted immediately with cold water (water/ash weight ratio = 0.16) and then a second stage in which the pressure of receptacle increased and the temperature reached the range from 130°C to 250°C due to the vaporization of the excess water and heating from both the heaters placed about the reactor and from heat release due to the conversion of quick lime to portlandite ($Ca(OH)_2$).

This 0.16 water/ash ratio was determined to ensure the complete conversion of the quick lime and to ensure the generation of a saturated steam atmosphere in the closed receptacle during the second stage of the hydration treatment. A smaller water/ash ratio did not allow complete hydration and a larger water/ash ratio caused some difficulties when stirring the paste during the first stage and in drying the hydrated ashes without attacking silicates and aluminates.

Constant stirring was maintained during all the treatments in the reactor used for hydration, both during the first stage to ensure the best and the quickest mixing of water with ashes, during the second stage to ensure uniformity of the temperature and therefore complete chemical conversion and also after opening the reactor in order to ensure the complete evaporation of the excess water prior to emptying the reactor..

As the batches were performed at the 3 to 5 kg level, after the hydration treatment, all the ash batches from the same source were mixed together, weighted and sampled.

- Hydrated bed ashes (PC1) : weight = 25 kg
  CERCHAR sample references 9742 & 9743

- Hydrated fly ashes (PC1) : weight = 75 kg
  CERCHAR sample references 9745 to 9748

- Hydrated fly ashes (PC3) : weight = 100 kg
  CERCHAR sample reference 9750 to 9753

Samples of about 1 kg were then taken and divided into 4 parts ; three were sent to the University of Toronto, to CNRS-CRMD of Orléans, and also kept at the CERCHAR laboratories for analysis. The 4th sample fractions were saved as reference materials.

The three pails of ashes, which had a total combined weight of approximately 200 kg hydrated ashes, were sent to CANMET at the end of March 92.

## HYDRATION DEGREE DETERMINATION BY CERCHAR

This task also concerned chemical analysis and physical changes in hydrated ashes.

At the moment CERCHAR's methods for determining the total degree of hydration comprise the following :

- a direct, but not quantitative, method carried out experimentaly by CNRS-CRMD (Centre National de la Recherche Scientifique - Centre de Recherche de la Matière Divisée à Orléans - France) [Mr. M. Crespin]. This method consists of passing the samples through a SIEMENS D500 X-Ray analyser under the same conditions and focusing on a single peak of quick lime XRD patterns and then comparing the non-dimensional surfaces. The results are given in the Table 2.

- an indirect and quantitative method carried out routinely by the University of Toronto, Ontario, Canada [Dr A. Iribarne]. The method determines the quick lime content by means of the difference between the free lime titration (quick lime and slaked lime contents expressed as CaO) and the slaked lime content (expressed as CaO), calculated by the $H_2O$ loss weight at 440°C under nitrogen atmosphere with a TGA balance. As CERCHAR has also a high pressure TGA, used for char characterization, the experimental procedure carried out by the University of Toronto was duplicated by CERCHAR. However, the determination of free lime was carried out following the French standard. The differences with the University of Toronto results are discussed. The results are given in the Table 1.

The X-Ray diffraction method and the chemical analysis are compared for both quick lime (Figure 4) and hydrated lime (Figure 5) determinations.

The measurement of physical changes were carried out by CERCHAR on a CILAS 715 laser using a particle sizing technique. The curves are drawn in the figures 1, 2 & 3. To achieve the best physical characterization, CERCHAR also investigated the BET specific surfaces on a MICROMERITICS ACCUSORB analyser, the Blaine specific surfaces, and the average particle specific gravity values on a MICROMERITICS AUTOPYCNOMETRE 1320.
The results are given in the Table 3.

As a matter of routine, loss on ignition under an air atmosphere at 40°C, 105°C and 1000°C were carried out by CERCHAR to confirm that the hydration process did not form ettringite and delivered a dry product (free water content less than 0.5%). The results are given in the Table 2.

**Mrs IRIBARNE' ANALYSIS**

It was decided to subcontract a part of this work to Mrs. Iribarne of the University of Toronto, to confirm some results obtained by CERCHAR.

The samples were analysed "as received" (from CERCHAR), except for sample 9741, which was previously ground to 200 mesh.

The results, referenced "Toronto", are given in the Table 1.

Two series of analysis were performed :

Titration of free lime - These analysis were done by the sugar method, following a modified ASTM-C25 norm. According to this norm, "the available lime index of high calcium quicklime and hydrated lime designates those constituents which enter into reaction under the conditions of this specified method. The interpreation of results obtained by the method shall be restricted by this definition." Therefore, the free lime content is the total amount of the calcium oxide, CaO, designated as quick lime, and the calcium hydroxide, $Ca(OH)_2$, designated as slaked lime or hydrated lime." The free lime determination, expressed as the CaO weight content, is the percentage of these calcium compounds in the dry sample analysed. Three of the samples were analysed in duplicate, and four of them in triplicate, as it seemed advisable given past results. The duplicate and triplicate results were consistent, within the experimental errors ; in these cases, the average values were taken.

Thermogravimetric analysis - The instrument used was a Dupont 951 Thermogravimetric Analyser, with Thermal Analyst 2000, and the experiments were run with oxygen-free nitrogen, with a heating rate of 25°C/mn, between < 100°C and 800°C or 1000°C. The $N_2$ flow rate was 50 ml/mn.

The analysis was focused on the data for $Ca(OH)_2$ (loss of water between 380°C and 450°C), and in 8 of the diagrams the region between 300°C and 600°C was recorded in amplified form, so as to obtain a better accuracy for the measurement. The measurements were taken by extrapolating the slope of the weight loss curve before and after the weight loss observed in the region of maximum slope (i.e. the peak of derivative curve), and determining the difference between the extrapolations at the temperature of that maximum.

**Mrs IRIBARNE' COMMENTS**

A small negative value for CaO % of sample 9743 is obviously due to experimental error, and must be interpreted as a small CaO content, probably between 0 and 1%.

No traces of $Mg(OH)_2$ have been observed in the TGA diagrams.

An increase in weight has been observed in the TGA readings after the loss of water associated with $Ca(OH)_2$. This is very pronounced for samples 9745 to 9748 and less so (although still substantial) for samples 9750 to 9753. As oxygen-free nitrogen was used in the determination, any residual oxygen that may be present (presumably in the order of parts per million) can hardly explain the increase as an oxidation. The weight increase therefore indicates absorption of $N_2$, and a similar absorption of argon has been verified in one analysis made under this gas ; the explaination is not obvious and may be related perhaps to a physical change and a phenomenon of adsorption. This remains as an unexplained feature in the present results.

**CERCHAR CHEMICAL ANALYSIS :**

Only the sample 9741 was previously ground to 200 µm before analysis.

The results, under the "CERCHAR" reference, are given in the Table 1.

Titration of free lime - These analysis were done by the sugar method following the French NF P 15 461 Standard. In spite of particle size reduction, the titration of the sample 9741 failed due to lack of reliability probably arising from the limited time of contact between the particles and the sugar solution, which did not allow complete digestion of the free lime compounds. To conclude, this digestion was continued for 24 hours so the result obtained was consistent with those obtained by Mrs. Iribarne. Nevertheless, we should be cautious of these results because it has been previously demonstrated that the French method was not effective for the Gardanne fly ash samples, due to the low solubility of the calcium species from the silicates and aluminates compounds.

Thermogravimetric analysis - The equipment belonging to CERCHAR was designed for high pressure and high temperature investigation on "char" characterization. The TGA were performed under nitrogen gas at a flow rate of 5 l/mn, with a heating rate of 10°C/mn from room temperature to 950°C. The weight of the samples analysed was about 5 g. Unlike Mrs Iribarne, CERCHAR has not yet used standard samples (such as calcium oxalate) for controlling its thermo-balance.

The analyses were focused on the weight loss curve around 440°C. The water loss was measured on the curve by drawing the tangents to the curve above 460°C and under 380°C and a vertical line segment between the two tangents, crossing the curve at its middle. By calculation, the water loss was then converted in $Ca(OH)_2$ expressed as CaO%. This calculation was carried out in conjunction with Mrs Iribarne after a discussion of her own results.

The weight losses at 40°C, 105°C were performed under air in a oven for 24 hours and then the loss on ignition at 1000°C were carried out for 15 mn on the samples, previously dried at 105°C, by using an electrical quartz furnace. The results are given in the Table 2.

**CNRS-CRMD X-RAY DIFFRACTION ANALYSIS**

As CERCHAR has no X-Ray diffraction analyser, the work was sub-contracted to the CNRS-CRMD which has substantial experience in this field of research.

The analysis were carried out under the same working conditions (CT:10.0s, SS:0.020dg, WL:1.5406Ao) on a SIEMENS D500 X-Ray diffraction analyser. Both slaked lime peak around 18°($2\theta$-Cu) and quick lime peak around 37.4°($2\theta$-Cu) were analysed and the surfaces calculated.

The results are given in the Table 2. We consider that a result close to zero means that no species has been found by this method.

The comparisons with the chemical methods are shown in figures 4 & 5.

**CERCHAR PHYSICAL CHARACTERIZATION**

The bed ashes particles size dimension distribution were carried out by dry sieving. The fly ashes particles size dimension distribution were carried out in isopropyl alcohol on a CILAS 715 laser technique counter. We took into account the quantity of coarse particles above 200 µm by a dry sieving method. The curves of the cumulative size fraction passing were drawn in the figures 1, 2 &3.

The BET and Blaine specific surfaces and the average particle specific gravity were also investigated and the results given in the Table 3. The BET specific surfaces were carried out on a MICROMERITICS ACCUSORB, the Blaine specific surfaces were obtained following the French NF P 15 442 Standard and the average particle specific gravity values were obtained using a MICROMERITICS AUTOPYCNOMETRE 1320.

Specific surface is considered as pore surface area calculated from the PV work expended in forcing mercury into the pores. The volume of mercury V penetrating the pores is measured directly as a function of applied pressure P.

**DISCUSSION OF THE RESULTS**

The three ashes are different in their chemical composition and their physical characteristics. This is the reason for reporting our discussion about the corresponding results separately.

The sole common result for the three ashes came from the loss on ignition at 105°C, which was less than 0.5% (Table 2). However, these results do not prove that there is no hydration of the anhydrous calcium sulfate. In the future, it would be better to performed the loss on ignition up to 200°C, which will include the transitions from gypsum to hemihydrate at 128°C and from hemihydrate to anhydrite at 163°C. Nevertheless, the TGA analysis results which did not show loss of weight up to more than 200°C allow us to conclude that there is a lack of sulpho-calcic attack of calcium aluminates or calcium silicates.

Our main purpose is to discuss the quick lime contents of the hydrated ashes given in the Table 1 and obtained by both Mrs. Iribarne, under the "Toronto" reference, and CERCHAR.

Bed ashes (PC1) - All of Mrs Iribarne' results were consistent in concluding that the quick lime component (20.5 ± 0.5%) of the "as received" ash (from CANMET) was converted to slaked lime by the treatment. The quick lime content release might be less than 1.5%. The physical characterizatics of the hydrated bed ashes, carried out by CERCHAR showed that they are completely converted. A lot of particles seemed to have been "blasted" by the treatment as showed in the figure 1.

Fly ashes (PC1) - Our conclusions about the physical changes are complicated by the high unburnt carbon content. With regards to the determination degree of hydration determination, the CERCHAR TGA analysis seemed in better agreement with the XRD analysis than Mrs Iribarne' analysis in confirming the effective complete hydration of the ashes. The "as received" quick lime component (10.5 ± 0.5%) were fully hydrated to slaked lime with a release of probably less than 1.5% of CaO.

Fly ashes (PC3) - Mrs. Iribarne and CERCHAR found about the same free lime content in the "as received" ashes (15.6% as quick lime) and in the hydrated ashes (15.8 ± 0.2%, expressed as CaO). Due to the conversion of CaO to $Ca(OH)_2$, we might have expected the hydrated ashes to have had an average free lime content value equal to 14.9%. Moreover, despite XRD patterns on which quick lime peaks determined were very small or completely absent, it is difficult to explain Mrs. Iribarne's results for the CaO chemical determination, given as 2.0 ± 0.5%. If Mrs. Iribarne's free lime determination for the hydrated ashes were overestimated by about 1%, then the unconverted quick lime content, calculated by CERCHAR as less than 1.5% of CaO, would be consistent with the XRD analysis.

**DISCUSSION OF THE METHODS**

At the present time there are no chemical methods available for the direct determination of the quick lime in presence of $Ca(OH)_2$, and other calcium species.

The chemical approach which consists of calculating the quick lime content by difference causes great difficulties when trying to explain the results from the hydrated ashes due to the small quantity of unconverted quick lime that we expect to see from the process of hydration.

The following results, mentionned in this discussion were obtained only by CERCHAR or CNRS-CRMD. No comparison were made with the results obtained by Mrs. Iribarne, however, the main conclusions here should remain unchanged.

In the figures 4 & 5, we have reported the results obtained by the XRD analysis and the chemical analysis for the quick lime content (CaO) and the slaked lime content ($Ca(OH)_2$) respectively.

Figure 4 showed a lack of reliability for the results when the quick lime contents were very low (less than 3% of CaO).

Figure 5 seemed to show a better agreement than figure 4, but the error for the hydrated lime values, expressed as CaO, is probably more than 2%. Therefore the errors for the calculated quick lime release content for the hydrated ashes may also be of the same order as the values themselves.

Table 1 : **Titration and TGA results**
All figures are % of sample

| Sample | | TGA $Ca(OH)_2$ expresed as CaO | | Free lime expressed as CaO | | Quick lime CaO by difference | |
|---|---|---|---|---|---|---|---|
| Type | No | CERCHAR | TORONTO | CERCHAR | TORONTO | CERCHAR | TORONTO |
| BA(PC1) | 9741 | 1.89 | 0.25 | 22.4 | 21.85 | 20.5 | 21.6 |
| BA(PC1) | 9742 | 18.75 | 19.3 | -- | 20.0 | -- | 0.7 |
| treated | 9743 | 19.74 | 20.0 | 21.0 | 19.8 | 1.3 | -0.14 |
| FA(PC1) | 9744 | 0 | <0.1 | 10.6 | 10.4 | 10.6 | 10.4 |
| FA | 9745 | 8.99 | 7.8 | 10.2 | 9.8 | 1.2 | 2.0 |
| (PC1) | 9746 | 9.16 | 7.6 | 10.0 | 9.8 | 0.8 | 2.2 |
| treated | 9747 | 8.68 | 6.2 | 10.1 | 9.9 | 1.4 | 3.8 |
| | 9748 | 9.43 | 7.5 | 10.0 | 10.0 | 0.6 | 2.5 |
| FA(PC3) | 9749 | 0.95 | <1.0 | 15.6 | 15.6 | 14.7 | 15.6 |
| FA | 9750 | 14.08 | 14.6 | 15.7 | 15.6 | 1.6 | 1.0 |
| (PC3) | 9751 | 13.34 | 13.5 | 15.7 | 15.8 | 2.4 | 2.3 |
| treated | 9752 | 13.72 | 13.9 | 16.0 | 15.5 | 2.3 | 1.6 |
| | 9753 | 13.40 | 14.4 | 16.0 | 15.4 | 2.6 | 1.4 |

Table 2 : **X-Ray Diffraction Analysis and Loss on Ignition** (% of sample)

| Sample | | XRD analysis non-dimensional peak surface | | Loss on ignition | | | |
|---|---|---|---|---|---|---|---|
| Type | No | CaO | $Ca(OH)_2$ | at 40°C | at 105°C | between 105°C and 1000°C | at 1000°C |
| BA(PC1) | 9741 | 99 | 2 | 0.14 | 0.21 | 0.14 | 0.35 |
| BA(PC1) | 9742 | 6 | 78 | 0.0 | 0.21 | 7.66 | 7.87 |
| treated | 9743 | 6 | 85 | 0.19 | 0.19 | 5.85 | 6.04 |
| FA(PC1) | 9744 | 42 | 0 | 0.3 | 0.54 | 28.33 | 28.87 |
| FA | 9745 | 0 | 24 | 0.2 | 0.4 | 29.49 | 29.89 |
| (PC1) | 9746 | 0 | 20 | 0.18 | 0.31 | 29.83 | 30.14 |
| treated | 9747 | 0 | 27 | 0.11 | 0.23 | 28.36 | 28.59 |
| | 9748 | 0 | 23 | 0.11 | 0.23 | 27.71 | 27.94 |
| FA(PC3) | 9749 | 57 | 1 | 0.1 | 0.29 | 18.2 | 18.49 |
| FA | 9750 | 1 | 42 | 0.1 | 0.3 | 19.6 | 19.9 |
| (PC3) | 9751 | 0 | 44 | 0.22 | 0.22 | 19.08 | 19.30 |
| treated | 9752 | 1 | 40 | 0.21 | 0.26 | 18.37 | 18.63 |
| | 9753 | 0 | 43 | 0.11 | 0.33 | 17.94 | 18.27 |

Table 3 : **Physical Characteritics**

| Sample | | BET specific surface cm2/g | Blaine specific surface m2/g | Specific gravity under Helium g/cm3 |
|---|---|---|---|---|
| Type | No | | | |
| BA(PC1) | 9741 | 0.798 | impossible | 2.943 |
| BA(PC1) | 9742 | 3.707 | 6,853 | 2.761 |
| treated | 9743 | -- | 5,264 | 2.647 |
| FA(PC1) | 9744 | 6.624 | 4,179 | 2.590 |
| FA | 9745 | 5.958 | 5,339 | 2.493 |
| (PC1) | 9746 | -- | 4,745 | 2.498 |
| treated | 9747 | -- | 4,967 | 2.572 |
| | 9748 | -- | 5,325 | 2.542 |
| FA(PC3) | 9749 | 4.240 | 2,965 | 2.747 |
| FA | 9750 | 4.716 | 4,762 | 2.546 |
| (PC3) | 9751 | -- | 4,256 | 2.581 |
| treated | 9751 | -- | 4,192 | 2.589 |
| | 9753 | -- | 4,182 | 2.560 |

Figure 1 : Particle size dimension distribution

CANMET bed ashes (PC1)

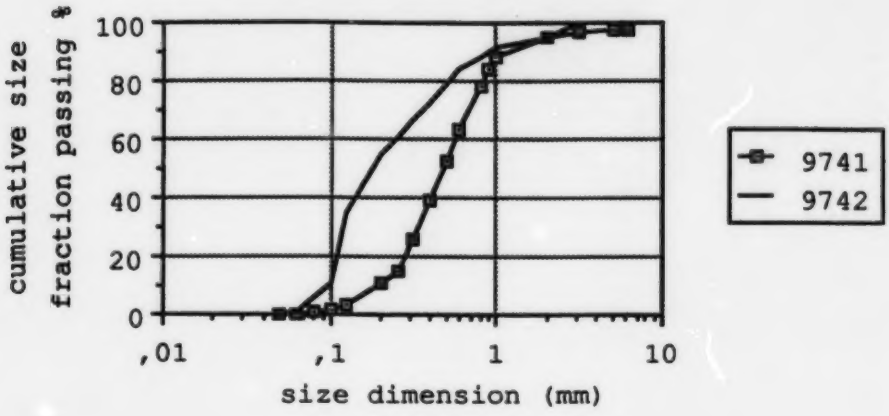


Figure 2 : Particle size dimension distribution

CANMET fly ashes (PC1)

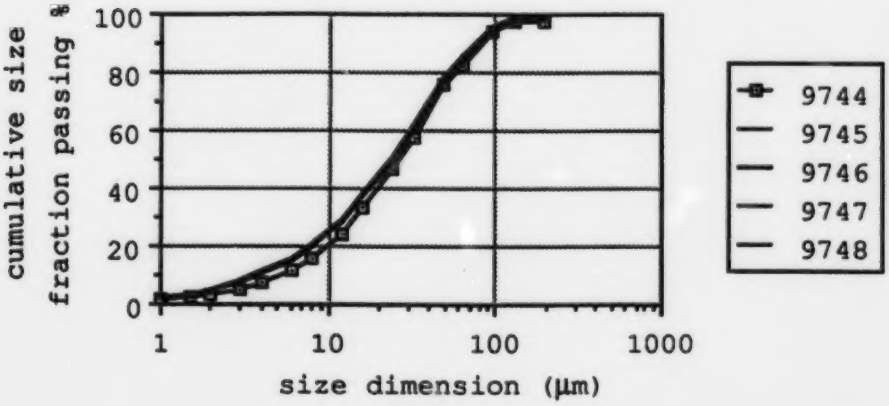


Figure 3 : Particle size dimension distribution

CANMET fly ashes (PC3)

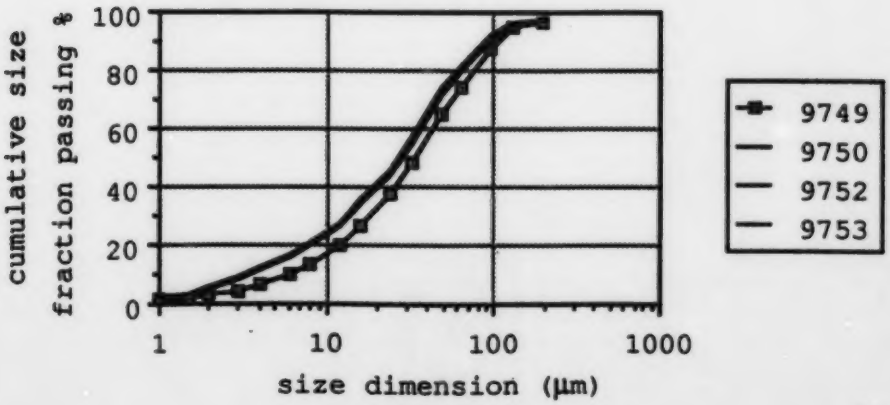

Figure 4 : Comparison between X-Ray diffraction analysis and indirect titration of quick lime content

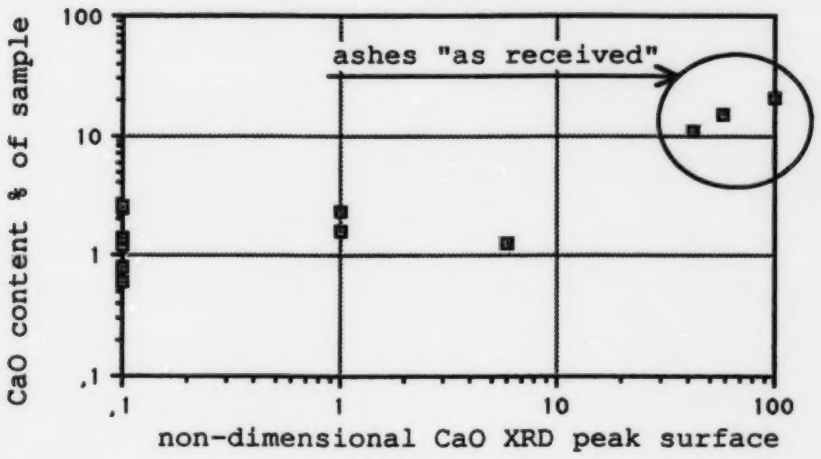


Figure 5 : Comparison between X-Ray diffraction analysis and TGA determination method